Belgian Science Policy Office
belspo

Universiteit
Antwerpen

Fundamentals of plasma-surface interactions

Friday 8 November 2013

Congress Centre ‘t Elzenveld, Antwerp, Belgium

Programme

08h30	Registration
09h00	Welcome address
09h10	**Mark Kushner** (University of Michigan, Electrical Engineering and Computer Science Department, Ann Arbor, MI, U.S.A.) *Plasma-surface interactions at inorganic, liquid and organic (living) surfaces: differences and similarities.*
09h50	**Francisco J. Aparicio Rebollo** (Université de Mons, Service de Chimie Inorganique et Analytique, Mons, Belgium) *Effect of deposition temperature on the composition and properties of propanethiol plasma polymer thin films.*
10h15	**Vanina Cristaudo** (Université Catholique de Louvain (UCL), Institut de la Matière Condensée et des Nanosciences (IMCN), pôle Bio & Soft Matter (BSMA), Louvain-la-Neuve, Belgium) *Chemical surface and 3D characterisation of plasma-treated and plasma-polymer films.*
10h40	Coffee break
11h10	**Thierry Dufour** (Université Libre de Bruxelles (ULB), Chimie Analytique et Chimie des Interfaces (CHANI), Brussels, Belgium) *Interactions between polyethylene or fluoropolymer surfaces and the reactive species of atmospheric* $Ar/O_2/H_2O$ *and* He/O_2 *plasma sources.*
11h35	**Achim von Keudell** (Ruhr-University Bochum, Institute for Experimental Physics II, Research Department Plasmas with Complex Interactions, Bochum, Germany) *Dynamic of film growth during high power pulsed magnetron sputtering (HIPIMS) of titanium.*
12h15	Lunch break
14h00	**J. Christopher Whitehead** (The University of Manchester, School of Chemistry, Plasma Chemistry Group, Manchester, Great Britain) *Plasma-catalysis for gas treatment.*
14h40	**Adrian Revel** (Université Paris-Sud, Laboratoire de Physique des Gaz et des Plasmas, Orsay, France) *Study of self-organizing structure in magnetron plasma discharge by pseudo 3D PIC MCC in HIPIMS regime.*
15h05	**Erik C. Neyts** (Universiteit Antwerpen, Research group PLASMANT, Antwerp-Wilrijk, Belgium) *Molecular dynamics simulations of plasma-surface interactions.*
15h30	Coffee break
16h00	**Joost J.A.M. van der Mullen** (Technische Universiteit Eindhoven, Department of Applied Physics, Elementary Processes in Gas Discharges, Eindhoven, The Netherlands) *Modelling the plasma-surface interaction in the racetrack region of a HiPIMS.*
16h25	**Diederik Depla** (Ghent University, Department of Solid State Sciences, Ghent, Belgium) *Tuning the microstructure of YSZ thin films.*
16h50	Concluding remarks
17h00	Cocktail reception offered by BELVAC on the occasion of its 50th anniversary

Fundamentals of plasma-surface interactions

Friday 8 November 2013

Congress Centre ‘t Elzenveld, Antwerp, Belgium

Practical information

The symposium is organized by the Research group PLASMANT of the University of Antwerp, in the framework of the IAP Network “Physical Chemistry of Plasma-Surface Interactions (PSI)”. Partners of this network are M.-P. Delplancke (coordinator), F. Reniers and G. Degrez (all ULB), R. Snyders (UMons), A. Delcorte (UCL), A. Bogaerts (UA), J. van Dijk (TU/e), and T. Minea (Université Paris-Sud).

This workshop is supported by IAP - PSI (Physical chemistry of plasma surface interactions (Belgian Federal Government BELSPO agency)).

This workshop is sponsored by the University of Antwerp’s Doctoral School Programme, and the University of Antwerp’s University & Community Department.

The organizers are grateful to BELVAC – Belgian Vacuum Society, DeMaCo Holland BV, Hositrad Vacuum Technology Holland BV, and Oerlikon Leybold Vacuum Nederland BV, for their support.

Fundamentals of plasma-surface interactions

Friday 8 November 2013

Congress Centre ‘t Elzenveld, Antwerp, Belgium

Abstracts of oral presentations

PLASMA-SURFACE INTERACTIONS AT INORGANIC, LIQUID AND ORGANIC (LIVING) SURFACES: DIFFERENCES AND SIMILARITIES

M.J. Kushner*
University of Michigan, Department of Electrical Engineering and Computer Science
1301 Beal Avenue, US-48109-2122 Ann Arbor, Michigan, U.S.A
* mjkush@umich.edu

Plasma surface interactions are indispensable in materials processing over a large range of applications and a wide range of pressures. Tremendous progress has been made in optimising reactive fluxes in low pressure plasmas to produce desired surface features in microelectronics fabrication. Trade-offs between damaging fluxes and rapid rates of etching or deposition are based on finer understanding of how incident reactive fluxes affect both the surface and sub-surface of the materials. These investigations continue to provide unexpected results. The recent discovery of VUV photon stimulated etching of Si in halogen plasmas and aging of low-k materials by VUV photons has refocused attention on the influence of plasma generated, short wavelength fluxes on materials processing (see figure 1). These low pressure processing techniques have been extended to sterilisation and deposition of biocompatible films in biotechnology.

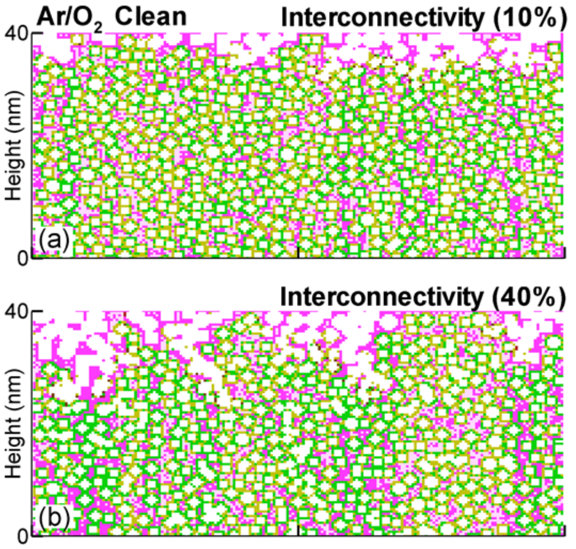

Figure 1. VUV induced, sub-surface damage in porous, low-k SiOCH dielectric for (a) low and (b) high interconnectivity of the pores.

At the other extreme is the use of atmospheric pressure plasmas for modification and functionalisation of polymeric materials. These processes are widely used in web-processing of commodity polymer sheets and are now being investigated for processing of high value materials in nano- and biotechnology. These systems are perhaps the most direct precursor for use of atmospheric pressure plasmas in catalysis, plasma medicine, environmental remediation and energy. The range of materials for plasma surface interactions now includes: metals, semiconductors and organic polymers, where the consequences of plasma surface interactions are typically desired only on the top surface; liquids and living tissue, where plasma surface interactions are intended to influence processes well below the surface (see figure 2); topographically simple surfaces where all sites have a view to the plasma; and topographically complex porous materials with surfaces hidden from the plasma.

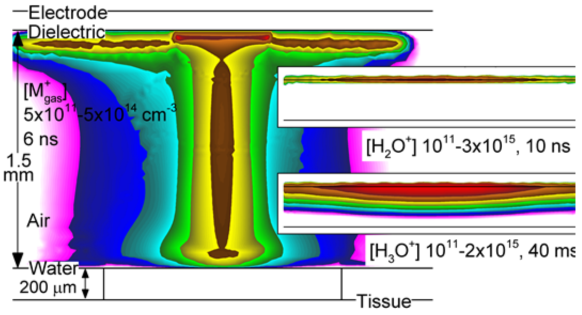

Figure 2. Positive ion densities during and after a DBD pulse sustained in humid air over a 200 μm water layer. (left) Total positive ion density in the gas phase at 6 ns into the pulse. (top enlargement) $H_2O_L^+$ at 10 ns in the liquid layer. (bottom enlargement) $H_3O_L^+$ at 40 ms.

In this presentation, we will discuss the common themes and clear differences in this broad range of plasma-surface interactions. Are there fundamental processes and knowledge that can be leveraged across these diverse applications?

Work supported by the US Dept. of Energy Fusion Energy Science, National Science Foundation, Semiconductor Research Corp. and Hewlett-Packard Research Labs.

EFFECT OF DEPOSITION TEMPERATURE ON THE COMPOSITION AND PROPERTIES OF PROPANETHIOL PLASMA POLYMER THIN FILMS

F.J. Aparicio[1,*], D. Thiry[1], P. Laha[2] and R. Snyders[1]
1 Université de Mons, Chimie des Interactions Plasma-Surface (ChIPS), CIRMAP
Place du Parc 20, BE-7000 Mons, Belgium
2 Vrije Universiteit Brussel (VUB), Electrochemical and Surface Engineering (SURF)
Pleinlaan 2, BE-1050 Brussels, Belgium
3 Materia Nova Research Center
Parc Initialis, Avenue Nicolas Copernic 1, BE-7000 Mons, Belgium
* francisco.aparicio@umons.ac.be

Synthesis of high refractive index ($n > 1.65$) polymeric films is a topic of interest for the implementation in advanced photonic devices [1, 2]. Due to their high molar refractions, the chemical polymerization of sulphur containing monomers is one of the approaches successfully used for the development of high refractive index material [1]. In this regards, the present work investigates the solvent-less synthesis of highly-sulphur-concentrated organic thin films by the plasma polymerization of propanethiol. The films were deposited in a radio frequency inductively coupled plasma reactor that can be operated in two different regimes denominated capacitive (E) and inductive (H) modes. Our first results revealed that the atomic sulphur concentration varies within a wide range (15 - 40 %) depending of the plasma mode [3]. Further mass spectra analyses suggest that such high concentration may be accounted by the preferential incorporation of sulphur based moieties. As a main novelty this work shows that this trapping process depends on the substrate temperature which in case H mode is strongly affected by the physicochemical processes at the growing-film/plasma interface. Experiments conducted at controlled temperature, with the help of an external cooling circuit, confirm both the proposed trapping scenario and the role of the substrate temperature on the synthesis of plasma polymeric films with high sulphur content. The acquired control enables to develop optical thin film with a controllable refractive index, from 1.69 to 1.82, being the latter one of the highest refractive index ever reported in organic materials.

References
[1] J.-G. Liu and M. Ueda (2009) *J. Mater. Chem.* **19** 8907-8919.
[2] F.J. Aparicio, M. Holgado, A. Borras, I. Blaszczyk-Lezak, A. Griol, C.A. Barrios, R. Casquel, F.J. Sanza, H. Sohlström, M. Antelius, A.R. González-Elipe and A. Barranco (2001) *Adv. Mater.* **23** 761-765.

CHEMICAL SURFACE AND 3D CHARACTERISATION OF PLASMA-TREATED AND PLASMA-POLYMER FILMS

V. Cristaudo[1,*], S. Collette[2], D. Merche[2], C. Poleunis[1], F. Reniers[2] and A. Delcorte[1]
1 Université Catholique de Louvain (UCL), Institut de la Matière Condensée et des Nanosciences (IMCN), pôle Bio & Soft Matter (BSMA)
1 Place Croix du Sud, box L7.04.01, BE-1348 Louvain-la-Neuve, Belgium
2 Université Libre de Bruxelles (ULB), Service de Chimie Analytique et Chimie des Interfaces (CHANI)
Campus de la Plaine, Boulevard du Triomphe 2, BE-1050 Brussels, Belgium
* vanina.cristaudo@uclouvain.be

The use of atmospheric plasmas for thin film deposition and surface modification of polymer materials has expanded enormously since the last decade [1, 2]. In addition to the many advantages offered by low pressure plasma techniques, atmospheric plasmas allow us to avoid the constraints of the vacuum. However, the chemical and physical properties of polymers treated or synthesized in atmospheric pressure discharges need to be better understood. With the advent of large noble gas clusters for 'damageless' sputtering and the excellent focus of Bi-cluster beams for imaging, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is now able to probe the structure and the local chemistry of these polymeric materials, via the elemental and molecular information present in the spatially resolved mass spectra [3]. Moreover, statistical data treatment methods, such as principal component analysis (PCA), significantly improve the amount of information that can be extracted from the SIMS measurements [4].

The present contribution illustrates the usefulness of ToF-SIMS characterisation with two case studies involving plasma-treated and plasma-polymer films:

1) *Chemical surface characterisation of plasma-treated LDPE (low density polyethylene) surfaces.* Water or deuterated water vapour is injected into the post-discharge of an argon atmospheric plasma torch. Several treatment times and sample-torch distances are investigated in order to observe the reactivity of the water vapour on the polymer surface. The ToF-SIMS characterisation of these samples indicates that the most important modification of the surface by the injected water occurs for a distance of 5 mm, because of the limited lifetime of the active species in the plasma.
2) *Molecular depth-profiling of plasma-polymerized fluorinated polystyrene thin films.* The synthesis is performed in a dielectric barrier discharge (DBD) from styrene and tetrafluoromethane vapour precursors, carried by Ar and He gas into the post-discharge. The chemical change along the depth of these polymer films corresponding to different deposition conditions, with varying times, powers and ratios between the two precursors, are investigated by soft depth profiling with large argon clusters.

References

[1] D. Merche, N. Vandencasteele and F. Reniers (2012) *Thin Solid Films* **520** 4219-4236.
[2] A. Bogaerts, E. Neyts, R. Gijbels and J. van der Mullen (2002) *Spectrochim. Acta B* **57** 609-658.
[3] C.M. Mahoney (2010) *Mass. Spectrom. Rev.* **29** 247-293.
[4] D.J. Graham and D. G. Castner (2012) *Biointerphases* **7** 1-12.

INTERACTIONS BETWEEN POLYMER SURFACES AND THE REACTIVE SPECIES OF ATMOSPHERIC Ar/O_2/H_2O AND He/O_2 PLASMA SOURCES

T. Dufour[*], S. Abou Rich, S. Collette and F. Reniers
Université Libre de Bruxelles (ULB), Service de Chimie Analytique et Chimie des Interfaces (CHANI)
Campus de la Plaine, Boulevard du Triomphe 2, BE-1050 Brussels, Belgium
* thierry.dufour@ulb.ac.be

To investigate plasma-surface interactions occurring at atmospheric pressure, polyethylene and fluoropolymer surfaces (PVF, PVDF, PTFE, FEP, PFA) have been exposed to different post-discharges. In this scope, the influence of the carrier (helium or argon) and reactive (oxygen or water vapour) gases are discussed on the plasma and surface properties. Under specific conditions (treatment time, plasma power, torch-to-substrate distance and flow rates), the oxidation and/or the roughening of the polymer surfaces can induce competitive and synergistic effects. These are highlighted by correlating plasma-phase diagnostics, namely optical emission spectroscopy (OES) and mass spectrometry (MS) with surface analysis techniques such as atomic force microscopy (AFM), Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) with the ability to eventually use the angle-resolved mode (AR-XPS).

After their plasma treatments, two families of polymers could be distinguished: the ones presenting carbon backbones (partially or totally) exposed to the post-discharge (LDPE, HDPE, PVF, PVDF) and the others with a carbon backbone entirely protected by F atoms (PTFE, FEP and PFA). In the case of pure helium post-discharge, a smoothing of the surface and very small mass losses are evidenced whatever the polymers, while a functionalisation is observed for polyethylene-like surfaces. In the He-O_2 post-discharge, we show that the morphology of the films has also changed due to a roughening of the surface (instead of the previous smoothing) with higher RMS values. Here again, the functionalisation of polyethylene is much important while it remains negligible for PTFE, FEP and PFA surfaces. Moreover, in accordance with the ejection of polymeric fragments from the surface, we have measured important mass losses in the case of PE, while they are negligible for the PTFE-like polymers. The active species of the pure He post-discharge (He metastable species, VUV radiation), of the He-O_2 post-discharge (O radicals, O_2* metastable species) and of the Ar/Ar-O_2 post-discharge induce therefore very different effects on the treated polymer surfaces.

As polyethylene is quite more degraded when exposed to any plasma treatment, whatever the nature of the carrier gas or even with/without O_2 mixed, it deserves a special interest to study the diffusion of oxygen into the bulk (from 0 to 50 nm) and to investigate the in-depth profile of hydroxyl (-OH), carbonyl (-C=O) and carboxyl (-COOH) groups responsible for the surface hydrophilicity. It is shown that, depending on the plasma conditions, oxygen could penetrate up to 20 - 40 nm into the LDPE during the atmospheric plasma treatment.

DYNAMIC OF FILM GROWTH DURING HIGH POWER PULSED MAGNETRON SPUTTERING (HIPIMS) OF TITANIUM

A. von Keudell*, C. Maszl, W. Breilmann and J. Benedikt
Ruhr-Universität Bochum, Institute for Experimental Physics II, Research Department Plasmas with Complex Interactions
DE-44780 Bochum, Germany
* achim.vonkeudell@rub.de

The temporal distribution of the incident fluxes of argon and titanium ions on the substrate during an argon HiPIMS pulse to sputter titanium with pulse lengths between 50 to 400 µs and peak powers up to 6 kW is measured by energy-resolved ion mass spectrometry with a temporal resolution of 2 µs. The data are correlated with time-resolved growth rates and with phase resolved optical emission spectra. Four ion contributions impinging on the substrate at different times and energies are identified: (i) an initial argon ion burst after ignition, (ii) a titanium and argon ion flux in phase with the plasma current due to ionized neutrals in front of the target, (iii) a small energetic burst of ions after plasma shut off, and (iv) cold ions impinging on the substrate in the late afterglow showing a pronounced maximum in current. The last contribution originates from ions generated during the plasma current maximum at 50 µs after ignition in the magnetic trap in front of the target. They require long transport times of a few 100 µs to reach the substrate. All energy distributions can be very well fitted with a shifted Maxwellian indicating an efficient thermalisation of the energetic species on their travel form target to substrate. The energy of titanium is higher than that of argon, because they originate from energetic neutrals of the sputter process. The determination of the temporal sequence of species, energies and fluxes in HiPIMS may lead to design rules for the targeted generation of these discharges and for synchronized biasing concepts to further improve the capabilities of high power impulse magnetron sputtering processes.

PLASMA-CATALYSIS FOR GAS TREATMENT

J.C. Whitehead*
The University of Manchester, School of Chemistry
Manchester M13 9PL, Great Britain
* j.c.whitehead@manchester.ac.uk

In this presentation, we examine the application of the combination of non-thermal, atmospheric pressure plasma with catalysts to provide a process for the treatment of waste gases including organic waste such as VOCs. Additionally, the effect of reforming of hydrocarbons to give syn gas and hydrogen will be examined using both dielectric barrier and gliding arc discharge. Particular attention will be paid to two aspects of the combination of plasma and catalysis. Firstly, how the combination can give a synergistic improvement in performance in terms of conversion efficiency and selectively and how this is related to the modification of the discharge characteristics by the addition of the catalyst into the discharge region and how the discharge may modify the properties of the catalyst. Secondly, we will discuss how the chemistry both in the gas-phase and upon the surface behaves in this hybrid environment and how different chemically-active and plasma-excited species behave.

Homepage: http://people.manchester.ac.uk/~mbdsszjw/

STUDY OF SELF-ORGANIZED STRUCTURES IN MAGNETRON PLASMA DISCHARGE BY PSEUDO 3D PIC-MCC IN HIPIMS REGIME

A. Revel* and T. Minea
CNRS - Université Paris-Sud, Laboratoire de Physique des Gaz et Plasmas
FR-91405 Orsay Cedex, France
* adrien.revel@hotmail.fr

HiPIMS (High Power Impulse Magnetron Sputtering) regime is gaining more and more impact due to its improved effectiveness to achieve tailored thin film. This is the consequence of the high plasma density increase, which sputter efficiently the target, ionize the sputtered species and finally leads to a raise of the ion bombardment on the substrate.

However, the strong interdependency between the different physical phenomena (electromagnetic field, diffusion, ionisation, etc...) is not well understood. Furthermore, recent experimental works related on self-organized plasma structures, called “spokes”, moving in the azimuthal direction whereas it should be uniform along the racetrack.

In order to have better understanding of the plasma, an improved 2D PIC-MCC (Particle in Cell - Monte Carlo Collision) code has been developed at LPGP to properly simulate the plasma behaviour in a magnetron discharge in both HiPIMS and DC regime. The simulated plane contains the symmetry axis and the lateral dimension (perpendicular to the racetrack).

The fast increase of the plasma density during the pulse drastically decreases the Debye length (15 µm) and consequently the accurate treatment requires very small mesh size. It follows an important number of nodes and an increase of the computation time. To reduce it, a non-uniform mesh has been implemented. The mesh is more refined where the plasma density is higher.

However, spokes modelling require the self-consistent treatment of the azimuthal direction, including the 3rd dimension. Nevertheless, a full 3D code is again very time consuming. Instead, we developed a pseudo 3D PIC-MCC code. It uses the results obtained by the 2D code to have the axial and radial electric field whereas the azimuthal one, only created by the plasma space charge, is calculated self-consistently by the pseudo 3D code.

This approach gives very interesting results. They show plasma structures moving along the azimuthal direction despite the uniform emission of secondary electron from the cathode by ion impact. These structures behave very alike to experimental identified 'spokes' leaving the magnetic trap region close to the target as plasma flares, at nanosecond scale. Furthermore, at µs scale, the plasma seems uniform as observed by fast camera measurements.

MOLECULAR DYNAMICS SIMULATIONS OF PLASMA-SURFACE INTERACTIONS

E.C. Neyts[*], J. Minnebo and A. Bogaerts
University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, BE-2610 Antwerp-Wilrijk, Belgium
* erik.neyts@uantwerpen.be

Plasma processing of materials offers numerous advantages over thermal processing, including lower operating temperatures, higher reactivity and improved resulting material properties [1]. Many bottlenecks, however, remain, including avoiding undesired side reactions or less controlled processing.

Key to improving plasma processing is a fundamental understanding of the reactive system. We employ hybrid reactive molecular dynamics / force bias Monte Carlo simulations [2] to study a variety of reactive systems on the atomic level, specifically in the context of plasma processing.

In this lecture, three specific topics will be covered. First, it will be discussed how the growth of carbon nanotubes can be steered and manipulated by the judicious use of plasma parameters such as the electric field and ion bombardment. Recent simulation results will be presented, demonstrating how the nucleation and growth of carbon nanotubes (CNTs) can be optimized in a plasma setup. We found that applying a sufficiently strong electric field, single walled CNTs nucleate vertically, aligned with the electric field, in agreement with experimental results. We propose a mechanism based on a competition between random thermal diffusion and directed migration of the carbon atoms in the nanocatalyst [3].

Further, we demonstrate that by bombarding a nucleation CNT-cap with ions having an energy in the range 10 - 25 eV, the nucleation of the cap is effectively enhanced. We explain this by an ion-induced carbon network reorganization mechanism [4]. Moreover, we also demonstrate that ion bombardment during the growth of the CNT allows to reduce the growth temperature [5].

Second, recent results will be presented on our simulations of plasma catalysis, with specific focus on hydrogen production from a methane plasma. We found that hydrogen formation may be optimized increasing the temperature of the catalyst. However, this eventually also leads to catalyst deactivation due to dissolving carbon into the catalyst [6, 7]. Finally, a number of difficulties that arise in this type of atomistic simulations will be discussed, as exemplified by the simulation of plasma functionalisation of polymers and the simulated contact angle measurement of water droplets on functionalized polyethylene.

References

[1] K. Ostrikov, E.C. Neyts and M. Meyyappan (2013) *Adv. Phys.* **62** 113-224.
[2] M.J. Mees, G. Pourtois, E.C. Neyts, B.J. Thijsse and A. Stesmans (2012) *Phys. Rev. B* **85** 134301.
[3] E.C. Neyts, A.C.T. van Duin and A. Bogaerts (2012) *J. Am. Chem. Soc.* **134** 1256-1260.
[4] E.C. Neyts, K. Ostrikov, Z.J. Han, S. Kumar, A.C.T. van Duin and A. Bogaerts (2013) *Phys. Rev. Lett.* **110** 065501.
[5] M. Shariat, S.I. Hosseini, B. Shokri and E.C. Neyts (2013) *Carbon* **65** 269.

[6] W. Somers, A. Bogaerts, A.C.T. van Duin and E.C. Neyts (2012) *J. Phys. Chem. C* **116** 20958.

[7] W. Somers, A. Bogaerts, A.C.T. van Duin, S. Huygh, K.M. Bal and E.C. Neyts (2013) *Cat. Today* **211** 131.

MODELLING THE PLASMA-SURFACE INTERACTION IN THE RACETRACK REGION OF A HIPIMS

K. Iordanova, G. Degrez and J.J.A.M.van der Mullen*
Université Libre de Bruxelles (ULB)
Campus de la Plaine, Boulevard du Triomphe 2, BE-1050 Brussels, Belgium
* jjamvandermullen@gmail.com

The task of the magnetic (B-) field in magnetron sputtering is to trap the electrons in a region just above the target. This enhances the degree of ionisation in that region and creates a sort of plasma reservoir. From this reservoir ions are launched via a sheath towards the target, the surface subjected to sputtering. Especially the region where the B field lines are parallel to the target will form a high density plasma. The area on the target just below that region is known as the race track.
The basic idea of high power impulse magnetron sputtering (HiPIMS) is to apply high power pulses of short time durations. As a result the plasma density is increased from $n_e = 10^{15}$ m^{-3} for conventional DC magnetron sputtering to above 10^{19} m^{-3} for HiPIMS. Advantages of HiPIMS are the uniform deposition of structures with high aspect ratios, interface modification through ion irradiation and increased film density. However, there are also disadvantages that are, among others, associated to the fact that huge instabilities can develop. To get a better understanding of the HiPIMS, in-depth studies are indispensable and one of the approaches is offered by modelling.
This talk will present the results of modelling as performed with a 2D model constructed with the PLASIMO toolkit. The sputtering mechanism was developed and implemented in the toolkit during the previous IAP project PSI by Diana Mihailova. Advantages of the PLASIMO approach is that changes in the model can easily be performed using the graphical user interface. In this way one gets insight in the importance of the various processes. This is further supported by the fact that the model convergences rapidly; typically in less than 15 minutes, provided smart model settings are employed.
Special attention is paid to the time-dependent behaviour of the plasma, the development of the sputtered material cloud in front of the target and how this influences the evolution of the plasma.
Results are compared with those obtained by the zero dimensional models of Wouter Graef [1]. These were also constructed with PLASIMO and inspired by the work of Gudmundsson [2].
It will be shown that especially the B-field confinement of the electrons is very essential but also that this mechanism is poorly understood.

References

[1] W.A.A.D Graef (2012) Zero-dimensional models for plasma chemistry. Ph.D.-thesis, Eindhoven University of Technology.

[2] J.T. Gudmundsson, J. Alami and U. Helmersson (2002) *Surf. Coatings Technol.* **161** 249-256.

TUNING THE MICROSTRUCTURE OF YSZ THIN FILMS

D. Depla*
Ghent University, Department of Solid State Sciences, Research Group DRAFT
Krijgslaan 281 (S1), BE-9000 Ghent, Belgium
*diederik.depla@ugent.be

Due to its mechanical strength, chemical stability, high ionic conductivity, low electrical conductivity, good radiation-resistance and low cost, YSZ has also become a popular material in different applications, e.g., as buffer layer, oxygen sensors, nuclear applications, solid state fuel cells and thermal barriers coatings. A good understanding of the microstructure and texture opens the possibility to manipulate its properties.

Magnetron sputter deposition is an industrial relevant technique which allows to change the microstructure and composition of thin films in a flexible way. In this paper the growth of YSZ thin films is studied under different experimental conditions with increasing complexity. So to kick start the discussion, a short overview of the growth of YSZ thin films under traditional conditions, i.e., a one source approach without substrate inclination. The experimental results can be summarized in a so-called structure zone model. Building on these results, the growth of biaxial aligned thin films will be shortly addressed. The influence of the substrate inclination will be discussed together with a simple model to explain the in-plane preferential orientation.

The presentation will end with an overview of the latest results on dual reactive magnetron sputter deposition of YSZ with different chemical composition. The variation of deposition conditions, such as pressure and Y target-substrate distance enables us to modify the film morphology and texture. The analysis of these films were performed in two steps: first, it involves the characterization of the film in a crystallographic way using X-ray diffraction (theta-2theta configuration), pole figures and cross section images via scanning electron microscopy and transmission electron microscopy. The preferential orientation of these films were studied and correlated with an extended structure zone model of the growing material. The columnar microstructure present in those films was fitted in a quantitative model where the columnar angle is related to the variation of composition along the sample and its correspondent grain size.

By reaching this level of understanding of the thin film growth, it is possible to tune the microstructure and morphology of the thin films by rotation of the sample holder. The paper will end with a few examples.

Fundamentals of plasma-surface interactions

Friday 8 November 2013

Congress Centre ‘t Elzenveld, Antwerp, Belgium

Abstracts of poster presentations

CHARACTERISATION OF THE DISSOCIATION OF CO_2/H_2O MIXTURES IN SURFACE-WAVE MICROWAVE DISCHARGES

G.X. Chen[1,3], T. Godfroid[2], R. Snyders[2,3] and M.P. Delplancke-Ogletree[1,*]
1 Université Libre de Bruxelles (ULB), 4MAT
Avenue F.D. Roosevelt 50, BE-1050 Brussels, Belgium
2 Materia Nova Research Center
Parc Initialis, Avenue Nicolas Copernic 1, BE-7000 Mons, Belgium
3 Université de Mons, Chimie des Interactions Plasma Surface (ChIPS)
Place du Parc 20, BE-7000 Mons, Belgium
* mpdelpla@ulb.ac.be

In view of gaining a basic understanding on the production of high-value chemical compounds by combining plasma activation and catalysis, we are studying H_2O/CO_2 mixtures. The first step of our strategy is to examine, the activation / dissociation pattern in absence of a catalyst in different plasma conditions.

In this work, we examine the dissociation of 50 % H_2O/ 50 % CO_2 mixtures in a pulsed surface-wave sustained discharge. The composition of the post-discharge is analyzed by gas chromatography using a thermal conductivity detector. The signals of H_2, O_2, CO and CO_2 are followed, depending on the discharge conditions. The investigated parameters are: the total flow rate, the residence time, the pulse duration for a fixed duty cycle, the energy provided per molecule and the total pressure. The dependence of the dissociation on these parameters is examined in details.

Preliminary data show that the optimum energy conditions for dissociating water and carbon dioxide are different. This could be related to the bond strength in the two molecules. On the other hand, an increase of the total flow rate reduces the average energy per molecule and thus lowers the dissociation rate. The influences of the pulse duration and residence time are complex and will also be detailed in the poster.

STUDY OF THE REACTIVITY OF WATER VAPOUR INTRODUCED IN THE POST-DISCHARGE OF AN Ar RF PLASMA TORCH - APPLICATION TO LDPE SURFACES

S. Collette[1,*], V. Cristaudo[2], T. Dufour[1], A. Delcorte[2] and F. Reniers[1]
1 Université Libre de Bruxelles (ULB), Service de Chimie Analytique et Chimie des Interfaces (CHANI)
Campus de la Plaine, Boulevard du Triomphe 2, BE-1050 Brussels, Belgium
2 Université Catholique de Louvain (UCL), Institut de la Matière Condensée et des Nanosciences (IMCN), pôle Bio et Soft Matter (BSMA)
Place Croix du Sud 1, BE-1348 Louvain-la-Neuve, Belgium
* scollett@ulb.ac.be

The study of the water reactivity in plasma was achieved by injecting water vapour in the post-discharge of an RF plasma torch operating at atmospheric pressure and supplied in argon as carrier gas. Production and consumption rates of Ar, O, OH, O_2^+ and N_2 species were evidenced by OES as a function of the water vapour flow rate, the treatment time and the gap (distance separating the post-discharge from a solid surface). We could therefore predict chemical reactions occurring within the post-discharge and weight their importance according to their kinetic constants, more specifically, in the case of the O and OH radicals.

An indirect method to evidence the reactivity of H_2O in the post-discharge was to expose LDPE (Low Density PolyEthylene) samples to the plasma torch and correlate the amount of oxygenated radicals resulting from water vapour dissociation reactions with the amount of oxygenated functions (C-O, C=O, COO) grafted on the surface. The modified LDPE surfaces were characterized by X-ray photoelectron spectroscopy, with a special emphasis on the deconvolution of the spectral envelope of the C1s peak. For longer treatment times, we also showed that the decrease in the oxygen concentration could result from a competition between the LDPE surface etching and its functionalization. Those results were correlated with WCA measurements indicating a decrease from 100° to 35°. A spatial resolution of the post-discharge was also performed to evaluate its dimension (between 7 and 8 mm vertically).

Furthermore, Tof-SIMS analyses were achieved by comparing the impact of H_2O and D_2O on LDPE surfaces, D_2O being used to probe the presence of oxygenated fragments issued from the post-discharge treatment and grafted on the LDPE surface.

This work was supported by IAP - PSI (Physical chemistry of plasma surface interactions (Belgian Federal Government BELSPO agency)).

SURFACE MODIFICATION OF Ti IMPLANT MATERIAL USING DIELECTRIC BARRIER DISCHARGES

P. Cools[1,*], N. De Geyter[1], E. Vanderleyden[2], F. Barberis[3], P. Dubruel[2] and R. Morent[1]
1 Ghent University, Faculty of Engineering, Department of Applied Physics, Research Unit Plasma Technology (RUPT)
Sint Pietersnieuwstraat 41 B4, BE-9000 Ghent, Belgium
2 Ghent University, Faculty of Sciences, Department of Organic Chemistry, Polymer Chemistry and Biomaterials Research Group (PBM)
Krijgslaan 281, BE-9000 Ghent, Belgium
3 University of Genua, Department of Materials Engineering and Building Sciences (DEUIM)
Piazzale Kennedy - Fiera del Mare - Pad. D, IT-16129 Genua, Italy
* pieter.cools@ugent.be

The modification and alteration of titanium for biomedical applications is a thoroughly studied area. Surprisingly, little to no research has been done on using plasma technology to improve the lifespan of titanium (hip) implants, although its usefulness has been proven for other biomedical applications. The goal of this work is to prove that plasma technology can be a useful addition as a pre-treatment for implants. In a first stage, the development of a new cleaning method for titanium surfaces is developed. A dielectric barrier discharge (DBD) at medium pressure operating in different atmospheres (air and argon) is used. The chemical and physical changes at the sample surface are studied, making use of contact angle measurements, X-ray photon spectroscopy (XPS) analysis and atomic force microscopy (AFM) measurements. The results of this study are then compared to other classic chemical and thermal treatments. These results show undoubtedly that the newly developed method is far superior in every aspect compared to the classic methods. Not only does it take only a fraction of the time, the cleaning itself is more thorough and the lack of solvents gives it a green character. Of all the different methods, only the thermal treatment matches the cleaning effectiveness of the plasma treatments, but it will also alter the atomic composition, resulting in a thick oxidized titanium layer. Compared to this, the plasma cleaning is considered non-invasive and can be labelled purely as a cleaning method. Of the two different atmospheres, the argon treatment is more effective, which is no surprise, as argon plasmas are known for their etching properties. In a second stage, the cleaned samples are coated with a plasma polymerised PMMA-nanolayer to improve the adhesion between the hydrophilic titanium implant and the hydrophobic PMMA bone-cement. Again a DBD is used, operating in a helium atmosphere at ambient pressure. Parameters such as treatment time, monomer gas flow and discharge power are varied one at a time. Chemical and physical changes are studied making use of XPS and AFM measurements. Coating thicknesses are recorded making use of optical reflectance spectroscopy. After characterisation, the coated samples are incubated into a phosphate buffer solution (PBS) for a minimum of one week at 37 °C, allowing to test the coating stability, when exposed to implant conditions. These simulations were done both for healthy and infected tissue. The results show that PMMA coatings can be deposited with a high degree of control concerning chemical composition and layer thickness. After incubation, all samples remain unaffected, making them suited for implantation. In a final stage all samples (uncleaned, plasma cleaned and plasma coated) are subjected to a pull-out test. All samples are cut to standard dimensions and immerged in a reproducible way with a newly developed sample holder. Both the cleaned and coated samples show a notable increase in adhesive strength and a sharp decrease in variance. These results prove indirectly that the plasma modifications lead to a more reliable implant material, with a longer implant life-time.

THE HIDEN EQP SYSTEM FOR MASS/ENERGY RESOLVED ANALYSIS OF PLASMA IONS, NEUTRAL AND RADICAL SPECIES

S. Davies*
Hiden Analytical Ltd.
420 Europa Boulevard, Warrington WA5 7UN, Great Britain
* sdavies@hiden.co.uk

There exist many plasma diagnostics but the most straightforward technique to determine fluxes of ions and neutral species is energy resolved mass spectrometry. It can be used to measure both negative and positive ions including short lived radical species formed in the atmospheric and low pressure plasma discharges. An overview of how a mass spectrometer works together with the latest scientific results on plasmas discharges obtained with energy resolved mass spectrometry from Hiden Analytical equipment will be presented.

SYNTHESIS OF ULTRA-POROUS CRYSTALLINE TiO_2 THIN FILMS BY GLANCING ANGLE REACTIVE MAGNETRON SPUTTERING

J. Dervaux[1,*], P.-A. Cormier[1], S. Konstandinidis[1] and R. Snyders[1,2]
1 Université de Mons, Chimie des Interactions Plasma-Surface (ChIPS), CIRMAP
Place du Parc 20, BE-7000 Mons, Belgium
2 Materia Nova Research Center
Parc Initialis, Avenue Nicolas Copernic 1, BE-7000 Mons, Belgium
* jonathan.dervaux@umons.ac.be

Nowadays, the efficient use of renewable energies represents a major economic and environmental issue. This is obviously also true for the solar energy, by far the most important one in term of quantity. In this context, among the many advantages of the dye sensitive solar cells, their cheap production cost is very interesting. Nevertheless, considering these cells, nowadays, the TiO_2 photo-anode often consists in nanoparticles that are difficult to recycle. A potential alternative the latter would be an ultra-porous crystalline TiO_2 thin film.

In this work, our aim is to evaluate the potentiality of the combination of reactive magnetron sputtering (MS) and glancing angle deposition (GLAD) in order to generate such a kind of porous coatings with a controlled crystalline constitution. The chemical composition, the crystalline constitution and the microstructure of the films are analyzed by XPS, XRD, SEM and AFM, respectively. The effects of the substrate temperature and of the bias voltage on the crystalline constitution and on the porosity of the films have been evaluated.

THE SYNTHESIS OF COPPER OXIDE THIN FILMS BY DC AND MPP PROCESSES

A. De Vreese[1,*], L. Mendizabal[2], S. Konstantinidis[1] and R. Snyders[1,3]
1 Université de Mons, Research Institute for Materials Science and Engineering, Chimie des Interactions Plasma Surface (ChIPS), CIRMAP
Place du Parc 23, BE-7000 Mons, Belgium
2 Tekniker
Calle Iñaki Goenaga 5, ES-20600 Eibar, Gipuzkoa Spain
3 Materia Nova Research Center
Parc Initialis, Avenue Nicolas Copernic 1, BE-7000 Mons, Belgium
* aurore.devreese@umons.ac.be

Much work has been done up to now regarding the deposition of metal oxides by ionized magnetron sputtering. However, very limited information regarding the plasma chemistry and the plasma-surface interaction during reactive MPPMS (Modulated Pulse Power Magnetron Sputtering) can be found. MPPMS is characterized by the possibility to generate micropulses within one overall macropulse. Through the variation of τ_{on} (duration of the micropulses) and τ_{off} (period between the micropulses) parameters completely different pulses can be created. The higher the τ_{on}/τ_{off} ratio, the stronger the discharge current and the ionisation rate are. In this study, copper is sputtered in reactive Ar/O_2 atmosphere using MPP power supply. Three different pulse waveforms have been used in order to change the peak current and then the plasma chemistry. The oxygen flow rate and the pressure are also varied to understand their influence on the system. The average power is kept constant and a conventional DC discharge is used as reference process. The deposition rate variation depending on the experimental parameters is measured. The influence of the deposition technology and the working conditions on the crystal structure has been analysed by X-ray diffraction (XRD). The morphology of the films has also been studied by scanning electron microscopy (SEM). Finally, the electrical properties have been measured.

The use of the MPPMS leads to a very different evolution of the target surface state when oxygen is added in the discharge (as compared to DC). The evolution of the critical oxygen flow (i.e., the amount of O_2 needed to form the oxide compound on the target surface) as a function of the pulse waveform is quite complex because of antagonistic effects: (i) the oxygen ion density is higher in MPPMS so the plasma reactivity is also increased (the critical flow is lowered), but (ii) the gas rarefaction at the target vicinity induced as the current is increased and the higher erosion rate will increase this critical flow. The obtained deposition rate was normalized by the calculated average power. It appears that, both in metallic and oxidized modes, the deposition rates are increased by using MPPMS. It should be explained by the increased erosion rate.

The analysis of the morphology in each condition shows that the columnar structure of copper oxides deposited in DC is replaced by a dense structure when MPP process is used. This is due to the increased energy brought to the growing films through intense ion bombardment. XRD analysis shows that, at constant oxygen flow rate, as the target current is increased, the XRD patterns of the deposited films exhibit peaks from CuO in DC conditions while Cu_2O and metallic copper peaks appear in the higher ionisation (i.e., discharge peak current) conditions. This observation could also be related to the increased erosion rate as the peak current become higher. Finally, the influence of these features on the electrical properties has been investigated.

DEPOSITION OF TITANIUM DIOXIDE THIN FILMS BY PULSED CATHODIC ARC TECHNIQUE: EFFECT OF SUBSTRATE TEMPERATURE AND DIRECT CURRENT BIAS

F. El Ghoulbzouri and M.-P. Delplancke-Ogletree*
Université Libre de Bruxelles (ULB), 4MAT
Avenue F.D. Roosevelt 50, BE-1050 Brussels, Belgium
* mpdelpla@ulb.ac.be

Titanium dioxide thin films were synthetized by pulsed cathodic arc in different conditions. The transition from amorphous phase to rutile phase is observed around a temperature of 673 K. A polycrystalline rutile phase could be obtained with a high hardness of 20 GPa and a Young modulus a 200 GPa at higher temperature. The application of a substrate bias voltage of -200 V and a substrate temperature of 873 K resulted in a textured sample. The combination of surface heating and high-energy ions allows the growth of rutile, the thermodynamically stable phase in these conditions. In addition, the application of bias induced a reduction of the threshold temperature for obtaining a crystalline phase to 473 K. The TEM micrographs revealed a narrow columnar microstructure which corresponds to the T zone in the structure zone model of Thornton. The grain sizes are of the order of 20 nm. We also studied the composition of the plasma by optical emission spectroscopy and mass spectrometry.

Ti I, Ti I, Ti III, Ti IV O I and O_2 II were identified in our plasma. The introduction of O_2 gas inside the chamber induced a decreasing of the total charge state of the generated plasma.

ZnO-Ag COMPOSITE BY REACTIVE MAGNETRON CO-SPUTTERING: STRUCTURAL AND MORPHOLOGICAL CHARACTERISATIONS

R. Francq[1,2,*], P.-A. Cormier[1] and R. Snyders[1,2]
1 Université de Mons, Research Institute for Materials Science and Engineering, Chimie des Interactions Plasma Surface (ChIPS), CIRMAP
Place du Parc 20, BE-7000 Mons, Belgium
2 Materia Nova Research Center
Parc Initialis, Avenue Nicolas Copernic 1, BE-7000 Mons, Belgium
* remy.francq@materianova.be

Nowadays, zinc oxide (ZnO) is extensively used as a semi-conductor for gas sensor or solar cell applications. It is accepted that doping ZnO films with Ag is a potential strategy to enhance its photocatalytic and antibacterial activities. Therefore, the controlled synthesis of ZnO-Ag thin films is of particular interest for medical use or for waste water purification. Nowadays, ZnO-Ag thin films are generally synthesized by wet chemistry methods (co-precipitation, sol-gel, hydrothermal, flame spray pyrolysis and electro-spinning) often using toxic solvents. Therefore, the development of less pollutant techniques would be of great interest for a large scale development of such a kind of coatings.

In this work, reactive magnetron co-sputtering is chosen as an efficient method to grow ZnO-Ag thin films. This approach allows a fine tuning of the the cristalline structure, morphology and stoichiometry of the films which are the main criteria defining the efficiency of the material in a given application. Our goal is to investigate the correlation between the experimental parameters of our process (applied power, pressure, target to substrate distance, oxygen flow rate) with the composition and the microstructure of the grown films.

The deposited films are characterized in terms of phase constitution (X-ray diffraction), microstructure (scanning electron microscopy), and chemistry (X-ray photoelectron spectroscopy).

THE PLASIMO PLASMA MODELING PLATFORM

W.A.A.D. Graef*, D. Mihailova, K.S.C. Peerenboom and J. van Dijk
Eindhoven University of Technology, Department of Applied Physics
Den Dolech 2, P.O. Box 513, NL-5600 MB, Eindhoven, The Netherlands
* w.a.a.d.graef@tue.nl

PLASIMO, an acronym that stands for PLAsma SImulation MOdel, is the name of the plasma modeling framework that has been under continuous development in the EPG plasma group at the faculty of applied physics of the Eindhoven University of Technology since the 90's of the previous century.

Since its initial form, aimed at modelling inductively coupled plasmas and cascaded arcs, it has gained much functionality catering to a plethora of plasma applications: LTE or non-LTE, steady state or transient, flowing or non-flowing, with or without space charges, 0D to 3D.

The platform, which is developed in C++, is characterized by a high degree of modularisation and offers a user friendly graphical user interface.

We present an overview of applications where this platform has successfully been employed.

EXPERIMENTAL AND THEORETICAL STUDY OF THE PLASMA-SURFACE INTERACTION DURING THE GROWTH OF ETHYL-LACTATE PLASMA POLYMERS

S. Ligot[1,*], F. Renaux[2], P. Raynaud[3], P. Gerbaux[4], M. Guillaume[5] and R. Snyders[1,2]
1 Université de Mons, Chimie des Interactions Plasma-Surface (ChIPS), CIRMAP
Place du Parc 23, BE-7000 Mons, Belgium
2 Materia Nova Research Center
Parc Initialis, Avenue Nicolas Copernic 1, BE-7000 Mons, Belgium
3 Université Paul Sabatier, Matériaux et Procédés Plasmas
118 route de Narbonne, FR-31062 Toulouse, France
4 Université de Mons, Groupe de Recherche en Spectrométrie de Masse
Place du Parc 23, BE-7000 Mons, Belgium
5 Université de Mons, Chimie des Matériaux Nouveaux, CIRMAP
Place du Parc 23, BE-7000 Mons, Belgium
* sylvie.ligot@umons.ac.be

By being (bio-)degradable and derived from renewable resources, polylactide (PLA) has gained enormous attention as an alternative to conventional synthetic packaging materials. Nevertheless, PLA presents significant water and gas permittivity which lead to a high degradation rate of the material by hydrolysis of the ester bonds limiting its potential applications in the packaging industry. In order to improve the barrier properties of PLA substrate, we propose to cover it with a cross-linked ethyl lactate-based plasma polymer film (ELPPF). The control of both chemical composition (ester bonds density) and cross-linking degree would allow tuning the gas permittivity and, as a consequence, the degradation rate of the PLA substrate [1].

In this work, in order to contribute to a deeper understanding of the growth mechanisms of the ELPPF, our objective is to correlate both plasma and film chemistries and, ultimately, to propose a clear picture of the plasma-surface interaction during the process.

ELPPF have been synthesized by PECVD using both continuous and pulsed RF power signal through an ICP copper coil. The applied power ranged between 5 and 400 W. The ELPPF chemistry, especially the ester function density, has been evaluated by the combination of chemical derivatisation and XPS measurements and compared to the plasma phase composition. The latter has been measured by using RGA mass spectrometry and in situ infrared spectroscopy. These data, supported by DFT calculations of gas phase reaction allow understanding the plasma phase chemistry and the plasma-surface interaction during ELPPF growth.

Our data reveal that, in the defined experimental window, we are able, by increasing the injected RF power, to tailor the ester content in the ELPPF from 1.4 to 18 at%. This trend is perfectly correlated to the plasma diagnostic data revealing the loss of the ester content with quite the same rate. Indeed, the in situ FTIR spectroscopy supported by the DFT theoretical vibrations allows to exactly identifying the ester vibration peak. Consequently, the intensity of this peak can directly be correlated to the ester content in the plasma. Finally, the mass spectrometry and FTIR data support the plasma polymer film chemistry evolution as a function of power.

References

[1] S. Ligot, F. Renaux, L. Denis, D. Cossement, N. Nuns, P. Dubois and R. Snyders (2013) Experimental study of the plasma polymerization of ethyl lactate. *Plasma Proc. Polym.*, accepted.

MODELLING BY KINETIC MONTE CARLO METHOD OF ENERGETIC ION BOMBARDMENT OF Si GROWING FILMS

S. Lucas[1,*], P. Moskovkin[1], V. Godinho[2], R. Álvarez[2], A. Palmero[2] and A. Fernandez[2]
1 Université de Namur, NAmur Research Institute for Life Science
Rue de Bruxelles 61, BE-5000, Namur, Belgium
2 CSIC-Universidad de Sevilla, Instituto de Ciencia de Materiales de Sevilla
Sevilla, Spain
* stephane.lucas@unamur.ac.be

A three dimensional kinetic Monte Carlo code NASCAM [1] developed originally to simulate and understand the mechanisms of surface nucleation has been further developed to simulate thick film growth (single layer or multi-layered system up to 100 nm).
The code includes deposition of given types of atom, diffusion, and energy transfer from incident atoms to the film. It can be used for simulating nucleation and growth of thin films, evolution of a given structure when annealed. It allows the simulation of millions of incident particles and the simulation of a system at high temperature without suffering large computational time. In this work this model was used to investigate the influence of energetic bombardment during film growth. To take into account energy transfer from incident atoms to the film a model was developed based on an assumption that on the approach to the surface an incident atom interacts with a group of atoms at the surface and thus all this atoms gain some energy from the projectile.
During the growth of the film a columnar structure can be obtained with a number of open and closed voids. This structure can be modified (densified) if energetic bombardment occurs during film growth. Using NASCAM, it is possible to predict how energetic ion bombardment may change the nanostructure of a growing film, its final density and surface roughness. In the particular case of rare gas bombardment during film growth, it is also possible to compute the amount of rare gas entrapped in the film structure.
Results of simulations are compared with experimental data (TEM, SEM, RBS) obtained by about the deposition of porous silicon coatings in an oblique magnetron deposition system.

References

[1] S. Lucas and P. Moskovkin (2010) *Thin Solid Films* **518** 5355-5361.

REACTIVE MOLECULAR DYNAMICS SIMULATIONS OF THE FUNCTIONALISATION OF POLYETHYLENE SURFACES BY OXYGEN ATOMS

J. Minnebo*, E.C. Neyts and A. Bogaerts
University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, BE-2610 Antwerp-Wilrijk, Belgium
* johan.minnebo@uantwerpen.be

Surface functionalisation of polymer materials using plasma processing is commonly used to improve their surface properties. To investigate the effects of the plasma on the polymer surface, molecular dynamics (MD) simulations of oxygen atoms impacting on a polyethylene film were carried out. Oxygen was chosen as this is believed to be the main plasma species responsible for the oxidation of the polymer surface. The results indicate that the oxygen atoms do not react immediately on impact, and thus are able to diffuse into the surface layer before reacting. Further simulations were performed to investigate the oxidative effects of oxygen atoms in the surface layer, focussing on the reaction mechanisms involved in polyethylene functionalisation. It was found that the prevalent reaction pathway involves an initiation reaction, where an oxygen atom breaks a carbon-carbon bond, leading to the formation of two new chain ends, with one oxygen radical attached to each end. Further oxidation happens more quickly on these activated sites, either by breaking the terminal carbon-carbon bond to split a formaldehyde molecule from the chain, or by abstracting a hydrogen atom at the terminal site to form an aldehyde group. This aldehyde, however, was not stable in the simulations and was quickly further oxidized and split from the chain. Due to the limited timescale of the simulations, the formation of new functional groups was not observed. In order to validate the reaction mechanisms, nudged elastic band (NEB) simulations were performed to calculate the reaction energy barriers for an oxygen atom reacting with a decane molecule. These calculations indicate that the energy barrier for the initiation reaction is higher than the barrier for further reactions, confirming the observation that reactions are more likely to take place at activated sites. However, the lowest energy barrier for an initiation reaction was found for hydrogen abstraction, which was not observed during the simulation of the oxidation of a polyethylene surface layer.

A MULTITECHNIQUE STUDY OF THE INTERFACIAL REACTION BETWEEN TiO_2 SURFACES AND MOLYBDENUM

X. Noirfalise[1,*], D. Cossement[2], N. Nuns[3], F. Renaux[2] and R. Snyders[1,2]
1 Université de Mons, Chimie des interactions Plasma Surface (ChIPS)
Place du Parc 20, BE-7000 Mons, Belgium
2 Materia Nova Research Center
Parc Initialis, Avenue Nicolas Copernic 1, BE-7000 Mons, Belgium
[3] Université Lille 1 Sciences et Technologies
FR-59655 Villeneuve d'Ascq, France
* xavier.noirfalise@umons.ac.be

Since a few years, molybdenum oxides have attracted a lot of interest due to their numerous applications such as catalytic materials, lubricants, memory devices, gas sensors and solid state microbatteries. On the other hand, TiO_2 surfaces supporting metals have generated a lot of works due to the strong relation between the morphology of the deposit and the electronic interactions between TiO_2 and the deposited metal.

In this work, we aim to grow, by non-reactive DC sputtering of a metallic Mo target, MoO_x films on TiO_2 supports differing by their crystallographic constitution (amorphous, anatase and rutile). Particular attention is made on the diffusion mechanism and oxidation process at the interface TiO_2/MoO_x using XPS and Tof-SIMS measurement.

Differences were found in this electronic exchange and, as a consequence, in the growth mode for the two TiO_2 substrates. The emphasis is made with the Cabrera-Mott theory, i.e., the dependence of the interface reaction on the bulk electronic structure of the two phases. Growth mechanisms were estimated using analysis of the peak and background shapes of the XPS signal using the "QUASES" software. For example, a layer by layer growth mode is observed for Mo deposited on the (110)-rutile TiO_2 substrate and a Stranki-Krastanov growth on the amorphous one. Tof-SIMS depth profile measurements reveal the diffusion of oxygen at the TiO_2/Mo interface with appearance of an oxygen depleted zone at the surface of the TiO_2 support.

STUDY OF THE REACTIVITY OF ATMOSPHERIC PRESSURE CO_2/H_2O PLASMAS

A. Ozkan[1,2,*], R. Snoeckx[2], G. Arnoult[1], T. Bieber[1], P. De Keyzer[1], A. Bogaerts[2] and F. Reniers[1]
1 Université Libre de Bruxelles (ULB), Service de Chimie Analytique et Chimie des Interfaces (CHANI)
Campus de la Plaine, Boulevard du Triomphe 2, BE-1050 Brussels, Belgium
2 University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, BE-2610 Antwerp-Wilrijk, Belgium
* alp.ozkan@uantwerpen.be

Carbon dioxide is usually considered as an end-product in chemistry because of its high stability. However, due to the high quantities of CO_2 produced, its conversion has received more and more attention in recent years.

The present work aims to study the reactivity of atmospheric plasmas composed of CO_2 and H_2O both experimentally as well as theoretically. So far, only a few studies have been dedicated to CO_2 and/or H_2O plasmas, due to their plasma-destabilizing behaviour. However, their potential reactivity could represent a promising approach in various applications such as the functionalization of polymer surfaces [1, 2]. The objective of this experimental and theoretical approach is to obtain a better understanding of the mechanisms related to the reactivity of CO_2/H_2O plasmas. The theoretical part is carried out by simulation via a 0D chemical kinetic model (Global_Kin [3]). For the experimental part, a cylindrical shaped Dielectric Barrier Discharge (DBD) plasma reactor is used for the treatment of CO_2 and water vapor in a continuous flow (Figure 1). The products are analyzed by a mass spectrometer to obtain the conversion rate of CO_2.

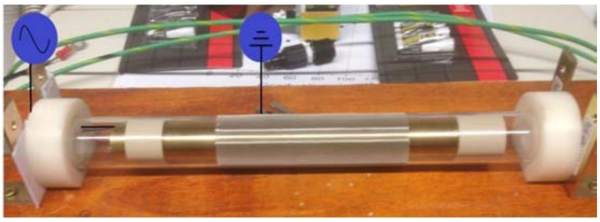

Figure 1. Picture of the tubular shaped DBD reactor.

CO_2 plasmas have been studied under different working parameters, with and without water vapour. It has been observed that CO_2 plasmas in absence of water always lead to a better conversion of CO_2 (Figure 2). This shows that water is an important destabilizer for the discharge since water highly tends to trap free electrons in the discharge. However, a small amount of H_2, which can be seen as a valuable product of plasma treatment, is always observed by mass spectrometry when the plasma also contains H_2O.

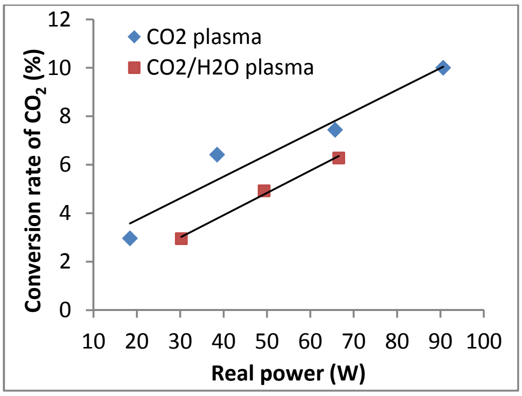

Figure 2. Conversion rate of CO_2 as a function of applied power for a CO_2 plasma in absence and presence of H_2O.

The effect of applied power has also been investigated, showing that the consumption of CO_2 and production of CO and O_2 become more important when increasing the input power. The different electron densities have been simulated according to the power injected in the discharge. It is observed that the electron density increases drastically with the increased power. Finally, the conversion rate of CO_2 as a function of the residence time has also been calculated by the model for two different powers used in the experiments. The calculated values of conversion rates are in good agreement with experimental values obtained in the same conditions.

References

[1] U. Kogelschatz (2003) *Plasma Chem. Plasma Process.* **23** 1-46.
[2] N. Médard, J-C. Soutif and F. Poncin-Epaillard (2002) *Langmuir* **18** 2246-2253.
[3] R. Dorai, K. Hassouni and M.J. Kushner (2000) *J. Appl. Phys.* **88** 6060-6071.

UNDERSTANDING THE PHASE FORMATION IN ZIRCONIUM OXIDE THIN FILMS

M. Raza[1,*], G. Geumez[1], T. Van Regemorter[2], R. Snyders[1,3] and S. Konstantinidis[1]
1 Université de Mons, Chimie des Interactions Plasma-Surface (ChIPS)
Place du Parc 23, BE-7000 Mons, Belgium
2 Université de Mons, Service de Chimie des Matériaux Nouveaux, CIRMAP
Place du Parc 23, BE-7000 Mons, Belgium
3 Materia Nova Research Center
Parc Initialis, Avenue Nicolas Copernic 1, BE-7000 Mons, Belgium
* mohsin.raza@materianova.be

In this work, the phase formation in zirconia (ZrO_2) thin films prepared by direct current (dc) reactive magnetron sputtering in argon/oxygen atmosphere has been studied. To investigate the role of film chemistry and discharge current in the phase formation of zirconia thin films, the films were grown in the transition zone (at the bottom, middle and peak of the transition zone) between the metallic and compound mode as well as in the poisoned mode by varying the oxygen partial pressure and thus controlling the target coverage with the help of target voltage feedback control unit at 200 mA and 400 mA. The pressure was kept constant at 5 mTorr. Optical emission spectra were also taken for various oxygen flows to characterize the plasma species and show the suppression of the zirconium emission lines with the increase in oxygen flow. To probe the Zr/O ratio in the films x-ray photoelectron spectroscopy (XPS) was used. The XPS analysis of the films grown in the transition zone at 200 mA show that the films are oxygen deficient and the deficiency lays up to 10 at% when deposited at the bottom of the transition zone. X-ray diffraction analysis of the films deposited at 200 mA was also performed and shows that tetragonal and cubic phase are formed when operated in the transition zone and monoclinic phase is formed when operated in the poisoned mode. Density functional theory (DFT) calculations revealed that by introducing the O vacancies in zirconia lattice above 5 at%, T/C phase tend to be thermodynamically more stable than monoclinic (M) phase. To investigate the influence of discharge current on phase formation of zirconia thin films, the films were also prepared at 400 mA in the transition zone (at the bottom, middle and peak of the transition zone) and in the poisoned mode. XRD analysis of the films shows that the increase in current altered the phase formation in zirconia thin films as compared to films grown at 200 mA. The results presented above show that the film chemistry and the discharge current play an important role in phase constitution of un-doped zirconia thin films.

RECENT PROGRESS IN MICROWAVE DISCHARGES DIAGNOSTICS FOR OPTIMISATION OF CO_2 DECOMPOSITION

T. Silva[1,*], N. Britun[1], T. Godfroid[2] and R. Snyders[1,2]
1 Université de Mons, Chimie des Interactions Plasma Surface (ChIPS), CIRMAP
Place du Parc 23, BE-7000 Mons, Belgium
2 Materia Nova Research Center
Parc Initialis, Avenue Nicolas Copernic 1, BE-7000 Mons, Belgium
* tiagodapontesilva@umons.ac.be

The recent results on the optical diagnostics of the flowing gas microwave CO_2-containing discharges working at 2.45 GHz in the pulsed and continuous regimes are presented. The pressure of the gas mixture during this work was about 10 Torr, while the plasma was sustained in the flowing CO_2 and CO_2+N_2 gas mixtures in a quartz tube crossing a waveguide [1].

The characteristic plasma temperatures, namely the gas temperature (via the N_2 and CO rotational temperatures), and N_2 vibrational temperature are determined as a function of time at different axial positions along the gas flow direction in the discharge tube. Besides this, the space-resolved measurements of CO_2 conversion rate through the discharge volume, as well as the measurements of plasma efficiency for such a conversion are performed using optical actinometry. For the last purpose, assuming low decomposition rate of molecular nitrogen during the plasma pulse, N_2 molecule is utilized as an actinometer [2, 3] to determine the CO density, as one of the products of CO_2 decomposition [4]. The validity of this method has been analysed for the described experimental conditions based on the assumption of a steady state of actinometric signal achieved during the discharge pulse.

The results of the time-resolved OES show a non-uniform dissociation rate of CO_2 that grows from the upper to the bottom part of the discharge tube, where it saturates. The dissociation degree is substantially modified by the variations of the power injected, the composition of the gas mixture and depending if the power supply operates in pulsed or continuous mode.

References
[1] T. Godfroid, J.P. Dauchot and M. Hecq (2003) *Surf. Coat. Technol.* **174-175** 1276.
[2] V.N. Ochkin (2009) *Spectroscopy of low temperature plasma*. (Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA).
[3] D.K. Otorbaev (1995) *Chem. Phys.* **196** 543-550.
[4] S.N. Andreev, V.V. Zakharov, V.N. Ochkin and S.Yu. Savinov (2004) *Spectrochim. Acta A* **60** 3361-3369.

PLASMA-BASED DRY REFORMING IN A DIELECTRIC BARRIER DISCHARGE: A COMPUTATIONAL STUDY

R. Snoeckx*, R. Aerts and A. Bogaerts
University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, BE-2610 Antwerp-Wilrijk, Belgium
* ramses.snoeckx@uantwerpen.be

Plasmas are used for various environmental applications. One of the most interesting ones, from both an economic and ecological point of view, is the conversion of greenhouse gases (mainly CO_2 and CH_4) into value-added chemicals or new fuels. We present a computational study for the conversion of CH_4 and CO_2, i.e., the so-called dry reforming of methane (DRM), in a dielectric barrier discharge (DBD). A zero-dimensional chemical kinetics model is presented, with the code Global_kin developed by Kushner and co-workers, to study the plasma chemistry for CH_4/CO_2 mixtures.

The central aim of this work is to describe the plasma chemistry occurring in a DBD for the dry reforming of CO_2/CH_4 mixtures. We seek a better understanding of the reaction kinetics, based on an analysis of the most important reactions, plasma species and operating parameters, via experimentally validated computer models. In this manner, we intend to find an answer to the question how the reaction chemistry looks like for real residence times and what the effect of varying the reaction parameters is, to eventually optimize the plasma-based dry reforming process for a DBD. The simulations are performed considering a large number of consecutive discharge pulses, to mimic the filamentary discharge regime of a DBD. In this way, we can obtain information on the conversion of the CO_2 and CH_4 gas molecules, as well as on the selectivity of the reaction products, and on the energy cost and energy efficiency of the process, which are of prime importance for this application.

With increasing Specific Energy Input (SEI) the conversions and yields increase, however, this higher conversion does not compensate for the higher energy input with regard to the energy efficiency. Thus, the highest energy efficiency is achieved for the lowest SEI value considered in this work. It is clear that H_2 and CO are the main reaction products; furthermore with increasing residence time (lower flow) the selectivity for these components increases. Also the selectivity of CH_3OH and esp. CH_2O are quite reasonable, and of great importance, since our simulations predict that these products can be formed directly.

Finally, the energy cost and energy efficiency of the process are found to be not yet competitive with the existing classical thermal DRM. Nevertheless, it should be mentioned that the process under study is far from optimized yet. However, it is well possible that a pure DBD reactor will never be competitive with the classical DRM. Therefore, in future work we will also investigate so-called plasma catalysis, as well as other types of plasma reactors, which are stated to be more energy efficient.

INTERACTIONS OF PLASMA SPECIES ON NICKEL CATALYSTS AS FUNCTION OF TEMPERATURE AND SURFACE TYPE: A REACTIVE MOLECULAR DYNAMICS STUDY

W. Somers*, A. Bogaerts, S. Huygh and E.C. Neyts
University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, BE-2610 Antwerp-Wilrijk, Belgium
* wesley.somers@uantwerpen.be

The potential use of hydrogen as a clean energy source has increased the attention towards the H_2 formation by Ni-catalyzed reforming of methane. Furthermore, this catalytic process can be combined with plasma technology, in order to obtain activation of the catalyst by the plasma. However, more fundamental knowledge of the complex mechanisms of this technique, referred to as plasma-catalysis, is required to make a breakthrough in environmental applications.

In this work, we investigate the interactions of CH_x ($x = \{1,2,3\}$) plasma species on nickel catalyst surfaces in a temperature range of 400 - 1600 K with reactive molecular dynamics (MD) simulations. These temperatures are typical for dielectric barrier discharges (400 K) and warm plasmas (1000 - 2000 K). We use the Reactive Force Field (ReaxFF) potential to describe the behaviour of all the atoms in the system [1]. Five different nickel catalyst surfaces are selected: Ni(111), which is the most stable and abundant nickel surface, Ni(100), which has a higher surface energy, a step-edged Ni(111) surface, denoted as sNi, an amorphous surface (aNi) and a polycrystalline surface (pNi). The polycrystalline surface is equally divided in a (111) and (100) structure, in order to study the interactions at the grain boundary.

At 400 K, CH_3 is found to simply adsorb on all surfaces, without further reacting, since adsorbed CH_3 is kinetically stable at such a temperature. This is in contrast with the high reactivity after CH_2 and CH impacts, for which new molecules such as CH_4 and C_2H_x are formed [2]. Furthermore, the observed reaction mechanisms are dependent of the surface. The H-atoms adsorbed on Ni(100) are subtracted by incoming radicals to form CH_4 and CH_3, while on Ni(111), the H-atoms remain adsorbed on the surface. The presence of steps in the surface increases the reactivity compared to a flat Ni(111) surface.

More importantly, H_2 is also formed, although the fraction is small at 400 K. However, if the temperature is sufficiently high, the energy barrier of 1.66 eV for the recombination of 2 H-atoms into a H_2 molecule is crossed. At 1600 K, roughly 4 %, 16 % and 12 % of the CH_3, CH_2 and CH impacts, respectively, are followed by H_2 formation, which makes it the most dominant reaction at this temperature [3]. Finally, the role of the nickel surface on the H_2 formation remains limited at such high temperatures. The increased carbon diffusion into the nickel surfaces lowers its crystallinity, and therefore, a proper distinction between the surfaces cannot be made.

We can conclude that H_2 formation is promoted by increasing temperature. Furthermore, the type of nickel surface initially influences the C-H bond breaking, but as the carbon diffusion in the surface increases, this role of the nickel surface becomes limited.

References

[1] J.E. Mueller, A.C.T. van Duin and W.A. Goddard (2010) *J. Phys. Chem. C* **114** 4939.

[2] W. Somers, A. Bogaerts, A.C.T. van Duin and E.C. Neyts (2012) *J. Phys. Chem. C* **116** 20958.

[3] W. Somers, A. Bogaerts, A.C.T. van Duin, S. Huygh, K.M. Bal and E.C. Neyts (2013) *Catal. Today* **211** 131.

A REACTIVE MOLECULAR DYNAMICS STUDY FOR PLASMA MEDICINE APPLICATIONS

M. Yusupov*, E.C. Neyts and A. Bogaerts
University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, BE-2610, Antwerp-Wilrijk, Belgium
* maksudbek.yusupov@uantwerpen.be

Plasma medicine is a research area of rapidly growing interest. It is based on the treatment of living and/or non-living surfaces with reactive species produced by cold atmospheric pressure plasma (CAPP) sources, which have been developed in recent years. Fields of application of the CAPPs include tooth bleaching, sterilisation of surfaces, treatment of skin diseases, etc.

Despite the growing interest in CAPPs for various biomedical applications, gaining control over the processes occurring in the plasma, as well as in the contact region of the plasma with the bio-organisms, still remains an open problem. It can be solved by using computer simulations that can provide fundamental information about processes occurring in the plasma (e.g., density distribution of plasma species, their reaction rates, etc.) and more importantly, at the surface of living cells (e.g., interaction of plasma species with bacterial cell wall, bond breaking events, etc.). Until now, however, very few modelling efforts have been made, especially with respect to the interaction of plasma with living organisms, such as bacteria (see e.g., [1-3]).

In the present work, we investigate the interaction of important plasma species, such as OH, H_2O_2, O, O_3, as well as O_2 and H_2O, with bacterial peptidoglycan (PG) by means of reactive molecular dynamics (MD) simulations based on the ReaxFF force field [4]. We assume the gram-positive bacterium *Staphylococcus aureus* murein as the PG structure. Our results demonstrate that OH, O, O_3 and H_2O_2 break structurally important bonds of PG (i.e. C-O, C-N or C-C bonds), which consequently leads to the destruction of the bacterial cell wall.

We also carried out a series of MD simulations to investigate the interaction of O and OH radicals with lipids, more specifically with α-linolenic acid as a model for the free fatty acids present in the upper skin layer. Our calculations predict that the O and OH radicals most typically abstract an H atom from the fatty acids, which can lead to the formation of a conjugated double bond, but also to the incorporation of alcohol or aldehyde groups, thereby increasing the hydrophilic character of the fatty acids and changing the general lipid composition of the skin.

Moreover, as living cells are typically surrounded by a liquid film, we also study the behaviour of the plasma species in liquid water in order to obtain more insight in their stability in the liquid, and hence in the probability that they can reach the living cells.

This study is important for gaining atomic-level insight into the mechanisms of plasma species interacting with bacteria, and in plasma disinfection in general.

References

[1] M. Yusupov, E.C. Neyts, U. Khalilov, R. Snoeckx, A.C.T. van Duin and A. Bogaerts (2012) *New J. Phys.* **14** 093043.

[2] M. Yusupov, A. Bogaerts, S. Huygh, R. Snoeckx, A.C.T. van Duin and E.C. Neyts (2013) *J. Phys. Chem. C* **117** 5993-5998.

[3] J. Van der Paal, S. Aernouts, A.C.T. van Duin, E.C. Neyts and A. Bogaerts (2013) *J. Phys. D: Appl. Phys.* **46** 395201

[4] A.C.T. van Duin, S. Dasgupta, F. Lorant and W.A. Goddard III (2001) *J. Phys. Chem. A* **105** 9396-9409.